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Density Functional Theory for the study of the multimode Jahn-Teller effect

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Abstract

The Jahn-Teller (JT) theorem states that in a molecule with a degenerate electronic state, a structural distortion must occur that lowers the symmetry, removes the degeneracy and lowers the energy. The multideterminental-DFT method performed to calculate the JT parameters for the JT active molecules is described. Within the harmonic approximation the JT distortion can be analyzed as a linear combination of all totally symmetric normal modes in any of the low symmetry minimum energy conformation, which allows calculating the Intrinsic Distortion Path (IDP), exactly from the high symmetry point to the low symmetry configuration. Results obtained by the approach described here give direct insight into the coupling of electronic structure and nuclear movements.

Key words: Intrinsic Distortion Path, Jahn-Teller Effect, Density Functional Theory

Introduction

"Quand un bébé pleure sans que l'on sache trop pourquoi, on dit que «ce sont les dents». De même dans la chimie des composés des éléments de transition, lorsqu'un phénomène expérimental ne peut être interprété facilement, on l'attribue bien souvent à l'effet Jahn-Teller. Et de fait, l'effet Jahn-Teller est tout à la fois source de réconfort et d'angoisse; réconfort parce qu'il est toujours là comme ultime recours pour expliquer un résultat, angoisse parce qu'il est bien difficile à mettre réellement en évidence, sans qu'il ne subsiste aucune ambiguité." [1]

Even though it passed over 70 years from the publication of the seminal paper of Jahn and Teller [2], the effect named after its authors continues to be a subject of interest in various fields of chemistry and physics. In a molecule with a degenerate electronic state structural distortion occurs that lowers the symmetry, removes the degeneracy and lowers the energy. At the high-symmetry (HS) nuclear configuration, Born-Oppenheimer approximation breaks

down. There is a vibronic coupling between the electron distribution and displacements of the nuclei. The theory underlying the Jahn-Teller (JT) and related effects is well known and documented in detail, e.g. in the book by Bersuker [3]. Quantifying the distortion and stabilization energy and getting insight into the mechanism is of great interest. Each chemical reaction starts with a perturbation of the electron distribution, which induces a movement of the nuclei leading to the reaction. Our interpretation of the JT distortion allows a direct insight into the coupling and contributes thereby to the understanding of the reaction pathways. The analogy between the JT distortion and reaction paths can be understood if one compares energy profiles along the typical reaction and the JT distortion (Fig. 1).

Figure 1

The transition state (TS) of a reaction corresponds to an energy maximum along the reaction coordinate and there will be a coupling between electron density and the movements of nuclei. A movement along the reaction coordinate, Q_a(RC), on the potential energy surface leads to the stabilization of the system by the destruction of the pseudomolecule and rearrangement of the nuclei into either reactants (R) or products (P). The chemical reaction is characterized with a set of parameters with a clear physical meaning: the activation energy (E_a), the reaction energy (E_r) and the reaction path (Q_a(RC)), Fig.1(b). Similarly the HS structure of the JT system corresponds to a cusp on the adiabatic potential energy surface. Vibronic coupling suppresses the crossing of the energy surfaces predicted in the BO approximation. By analogy the JT distortion can be described with: the JT stabilization energy (E_{JT}), the warping barrier (Δ) and the distortion path (Q_a(JT)), Fig. 1(a). The goal of the analysis of JT systems is the determination of these parameters. To achieve this it is necessary either to perform an experiment and fit the results to the proposed model, or today to carry out

a computational study. This is readily done using a multideterminental-Density Functional Theory (DFT) approach [4]. Recently we have extended the analysis of the JT distortion as a superposition of normal coordinates [5]. The essence of our model is to express the JT distortion as a linear combination of all totally symmetric normal modes in the low symmetry (LS) minimum energy conformation. This is in contrast to the usual treatment of the JT effect, which starts from the HS configuration. Our approach is based on the theory of chemical reactions of Bader [6], Pearson [7] and Fukui [8]. Any displacement on the potential energy surface has to be totally symmetric and consequently a superposition of the totally symmetric normal coordinates. Within the harmonic approximation the potential energy surface has a simple analytical form which allows calculating the path of minimal energy, Intrinsic Distortion Path (IDP), exactly from the HS point to the Low Symmetry (LS) energy minimum.

Methodology

Density Functional Calculations

The DFT calculations reported in this work have been carried out using the Amsterdam Density Functional program package, ADF2007.01 [9, 10, 11]. The local density approximation (LDA) characterized by the Vosko-Willk-Nusair (VWN) [12] parameterization have been used for the geometry optimizations. All electron Triple-zeta Slater-type orbital (STO) plus one polarization function (TZP) basis set have been used for all atoms.

Calculation of the Jahn-Teller Parameters

The JT effect is dictated by the molecular symmetry. The information from the group theory can be used for a qualitative discussion. This does not tell anything about the degree of the distortion or how big the energy gain is due to the distortion. The JT parameters, defined on

the Fig. 1. completely determine the adiabatic potential energy surfaces of the JT active molecules. The method for calculation of the JT parameters using DFT was developed in our group [4]. Briefly, it is necessary to know geometries and energies of the HS and the LS points to get the JT parameters. For the LS structure, as the system is in a non-degenerate electronic ground state, this is straightforward. Electronic structure of the HS point, on the other hand, must be represented with at least two Slater determinants, consequently, using a single determinant DFT is troublesome. A method based on the multideterminental-DFT, is therefore used.

This procedure consists of the following steps: i) average of configuration calculation in the HS point group. This yields the geometry of the high symmetry species. ii) A single-point calculation imposing the high symmetry on the nuclear geometry and the low symmetry on the electron density. This is achieved by introducing an adequate occupation scheme of the MOs. This gives the energy of a Slater determinant with an integer electron orbital occupancy. iii) A geometry optimization constraining the structure to the lower symmetry point group, with the same occupancy. E_{JT} is the difference between the energies obtained in the steps ii) and iii). Both steps are repeated for the other electronic states in the low symmetry point group.

Analysis of the multimode Jahn-Teller effect - Intrinsic Distortion Path

In a complex molecules, the JT distortion is a superposition of many different normal coordinates. Group theory allows finding the irreducible representation of the nontotally symmetric vibrations in the HS conformation, which are JT active, remove the degeneracy and lead to a stabilization of the system by lowering the symmetry. The irreducible representations of the active modes must belong to the same representation as the direct product of the components of the degenerate electronic state. The point group of the LS

minimum energy conformation is defined by the requirement that the irreps of the active modes become totally symmetric upon descent in symmetry and the application of the epikernal principle [3]. In the LS point group these modes might mix with a_1 vibrations which are always present in the direct product and never change upon descent in symmetry. In many situations other irreps in HS, which are not contained in the direct product, may become totally symmetric upon descent in symmetry and therefore contribute also to the JT distortion. In the JT semantics this is called the multimode problem.

Geometry of LS energy minimum is chosen to be the origin of the configuration space, $\vec{R}_{\mathrm{LS}} = \vec{0}$. Every point X on the potential energy surface can be represented by a $3N$ dimensional vector $\vec{R}_X$, using mass-weighted generalized coordinates relative to the origin.The potential energy surface within harmonic approximation is defined as a superposition of $N_{\mathrm{a1}} \leq 3N-6$ totally symmetric orthogonal oscillators in LS. As a consequence any displacement in the configuration space is given by a superposition of displacements along the totally symmetric normal coordinates. Thus, within the harmonic approximation it is possible to express $\vec{R}_X$ as a linear combination of N_{a1} totally symmetric normal coordinates in LS:

$$\vec{R}_{\mathrm{X}} = \mathbf{Q}\vec{w}_{\mathrm{X}} \qquad (1)$$

where $\vec{\omega}_X$ is the N_{a1} dimensional vector, containing the weighting factors, ω_{Xk} which represent the contribution of the displacements along the different totally symmetric normal coordinates to the $\vec{R}_X$; **Q** is the $3N$ x N_{a1} matrix with the columns being the $\vec{Q}_k$, totally symmetric normal coordinates which are the eigenvectors of the Hessian, obtained by the DFT frequency calculations in the LS minimum energy conformation. The corresponding eigenvalues are λ_k.

The energy of the nuclear configuration $\vec{R}_X$, E_X, relative to the LS energy minimum E_{LS} is expressed as the sum of the energy contributions of the N_{a1} totally symmetric normal modes:

$$E_{\mathrm{X}} = \sum_{\mathrm{k}=1}^{N_{a1}} E_{\mathrm{k}} = \frac{1}{2} \sum_{\mathrm{k}=1}^{N_{a1}} \omega_{\mathrm{Xk}}^2 \vec{Q}_{\mathrm{k}}^2 \lambda_{\mathrm{k}} \tag{2}$$

The force $\vec{F}_{Xk}$ driving the system to the LS energy minimum (origin) at any point $\vec{R}_X$ is defined as a derivative of the energy over the Cartesian coordinates. The total distortion force is given as a vector sum of the individual forces. In the HS point indicates the driving force for the JT distortion.

$$\vec{F}_{\mathrm{Xtot}} = \sum_{\mathrm{k}=1}^{N_{a1}} \vec{F}_{\mathrm{Xk}} = \sum_{\mathrm{k}=1}^{N_{a1}} \omega_{\mathrm{Xk}} \lambda_{\mathrm{k}} \mathbf{M}^{1/2} \vec{Q}_{\mathrm{k}} \tag{3}$$

where **M** is a diagonal 3*N* x 3*N* matrix with atomic masses in triplicates as elements (m_1, m_1, m_1, m_2, . . . , m_N). $\vec{F}_{Xtot}$, the force which drives the nuclei to the LS minimum gives the direction from one to the another point on the adiabatic potential energy surface in a way of maximizing decrease of the energy. Path from the HS to the LS minimum obtained in this way is the Intrinsic Distortion Path (IDP), which gives additional information about the microscopic origin and mechanism of the distortion. The vector $\vec{R}_{HS} - \vec{R}_{JT}$ defines the straight path (Direct Path) from the HS configuration to the LS energy minimum configuration. This is in general different from the IDP. The discrepancy between the two is smaller for the simpler systems, e.g. for Cu_3 and VCl_4. The contributions of the normal modes to the distortion are changing along the IDP. In the beginning the JT active modes that are the basis of the non-totally symmetric irreps in the HS point group are dominating. If there are

several appropriate vibrations, harder ones will be dominant in the first step, while the softer ones take over along the IDP. The contribution of the other modes is becoming more important for the direction of the relaxation with increasing deviation from the HS geometry. The contribution to the stabilization energy however is minor [13, 14].

Results and Discussion

Using multideterminental-DFT approach in the conjunction with IDP method, we analyzed the JT effect in different systems (Table 1). Details can be found in our previous papers [5, 13, 14, 15]. The considered molecules have a doubly degenerate electronic ground state, which is coupled with vibrations of a doubly degenerate irreducible representation in the HS point group, thus they belong to the $E \otimes e$ JT systems. On the other hand, these systems differ in the nature of chemical bonding, symmetry of the distortion, range of E_{JT}, the number of atoms, and hence the number of different normal modes that need to be considered in the IDP analysis. Thus, these systems are good test cases for our model of the analysis of the JT effect. Our approach to the multimode JT problem allows the determination of the JT parameters and the contributions of different normal modes to the distortion and to the $E_{JT.}$

Table 1

Among the simplest of JT molecules is Cu_3 cluster. It has a $^2E'$ electronic ground state in regular triangular nuclear configuration, D_{3h} point group. Using group theory it can be shown that distortion coordinate is e' and the distortion goes to C_{2v}. The electronic state will split into A_1 and B_2. Minima on the potential energy surface correspond to obtuse triangle geometry ($^2B_2$) while transition states to acute ($^2A_1$). The degenerate JT active distortion e' splits into a_1 and b_2. Only one component of the degenerate vibration is JT active. The JT distortion and the

JT stabilisation arise mainly from the *e'* type vibration (97% to the R_{JT}; 88% to the E_{JT}). It should be pointed out that a_1' normal coordinate in D_{3h} (breathing) in addition to the a_1' component of *e'* has a non zero gradient, although not lowering the symmetry, and it would be erroneous not to consider it [13].

VCl_4 is a tetrahedral molecule with a d^1 configuration. In T_d point group, a single electron occupies *e* orbital. The electronic ground state is ^2E. After the symmetry descent to D_{2d} the later splits into $^2A_1$ and $^2B_1$. In this case, only one mode dominates the distortion, contribution of the angle bending *e* mode to the distortion is more than 99%. In this case the classical model is sufficient to discuss the details of the JT distortion [4, 5].

The ground electronic state of cyclopentadienyl radical in D_{5h} symmetry is $^2E_1''$, with three electrons occupying the doubly degenerate orbital. The distortion coordinate is e_2'. The descent in symmetry goes to C_{2v}. The electronic state $^2E_1''$ splits into $^2A_2$ and $^2B_1$ and the JT active distortion e_2' splits into a_1 and b_2. Multideterminental DFT approach gives the value of 1253 cm^{-1} and IDP model value of 1238 cm^{-1} for E_{JT} which are in excellent agreement with the experimental one of 1237 cm^{-1} [17]. The three most important vibrations contributing to the JT distortion are C-C-C bend (24% to the R_{JT}; 20 % to the E_{JT}), C-C-H bend (53% to the R_{JT}; 20 % to the E_{JT}) and C-C stretch (6% to the R_{JT}; 54 % to the E_{JT}) [5].

JT instable metallocenes, e.g d^7 cobaltocene ($CoCp_2$) and low-spin d^5 manganocene ($MnCp_2$), are typical examples of the multimode JT distortions. The descent in symmetry goes from D_{5h} to C_{2v} (taking the eclipsed conformations of the rings). The internal rotation of the rings does not influence the JT distortion. The energy barrier upon rotation is much smaller than the JT stabilization. In C_{2v} minimum energy conformation, $CoCp_2$ and $MnCp_2$ have 16 totally symmetrical vibrations, which can all contribute to the distortion. The main contribution to the JT distortion in $CoCp_2$ arises from the four e_2' type vibrations: the out-of-plane ring distortion (65% to the R_{JT}; 59% to the E_{JT}), the in-plane ring distortion (11% to the R_{JT}; 15%

to the E_{JT}), the C-H wagging (12% to the R_{JT}; 8% to the E_{JT}), and in-plane C-H bending (8% to the R_{JT}; 7% to the E_{JT}). The JT distortion in $MnCp_2$, on the other hand, arises from two e_1' type and one a_1' type vibrations. e_1's are: skeletal-bending (79% to the R_{JT}; 22% to the E_{JT}) and ring-tilt (9% to the R_{JT}; 55% to the E_{JT}); a_1' is metal-ring stretch (10% to the R_{JT}; 12% to the E_{JT}) [5, 13, 15].

We analyzed all theoretically possible isomers of tris(ethylenediamine)copper(II) ($[Cu(en)_3]^{2+}$) in one absolute configuration: λλλ, λλδ, λδδ and δδδ. λλλ and δδδ isomers exibit D_3 symmetry. The Single Occupied Molecular Orbital (SOMO) belongs to irrep. *e* in D_3 point group and the descent in symmetry goes to C_2. Flipping the C-C backbone in one of the five-membered rings from λ to δ, or δ to λ respectively, reduces the symmetry to C_2. SOMO in these cases belongs to either *a* or *b* irrep. In order to have a comparation of the vibronic coupling in all the four isomers, for λλδ and λδδ geometry optimization was performed forcing both *a* and *b* orbitals to have 1.5 electrons. In this way we have obtained the geometry where the two states are degenerate, and all Cu-N bond lengths are the same. Although there are energy differences between the isomers of $[Cu(en)_3]^{2+}$, almost equal JT parameters suggests that conformation of the chelate ring does not affect the JT distortion. The minima on the potential energy surface for each isomer correspond to the tetragonally elongated octahedron. In C_2 energy minimum conformation $[Cu(en)_3]^{2+}$ has 53 totally symmetric normal modes. The skeletal vibrations are coupled with the vibrations of the chelate rings and the normal coordinate analysis is complicated. The results obtained by the IDP method are still in a good agreement with ones obtained by multideteminental DFT procedure, as well as with experimental value. We are able to distinguish four skeletal type modes which are the most important for the distortion: the N-Cu-N bending (23% to the R_{JT}; 5% to the E_{JT}), the two Cu-N stretching (58% to the R_{JT}; 57% to the E_{JT}) and the breathing mode (2% to the R_{JT}; 12% to the E_{JT}) [14].

Conclusion

The results presented in this paper demonstrate once more good ability of multideterminental DFT approach to predict the JT parameters, as well as corresponding geometries with a reasonable accuracy. This is of interest because the experimental determination of the JT parameters is often difficult. Furthermore, we have shown the analysis of the multimode JT effect using concept of the Intrinsic Distortion Path. Inspection of the path of minimal energy from the HS point towards the LS energy minimum gives the detailed information on the vibronic coupling, not possible to get from the experimental data. Conceptually simple model gives the direct insight into the one of the essential problems in the physical chemistry- coupling between the electron distribution and the motion of the nuclei.

Acknowledgements

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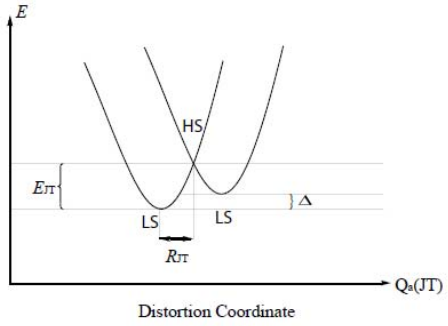
Table 1: Results of multideterminental-DFT calculations and IDP method performed to analyse the JT effect of selected compounds; E_{JT} and Δ are given in $10^3 cm^{-1}$; R_{JT} in $(amu)^{1/2}$Å; N is the number of atoms in a molecule; N_{a1} is the number of totally symmetrical vibrations in LS minimum

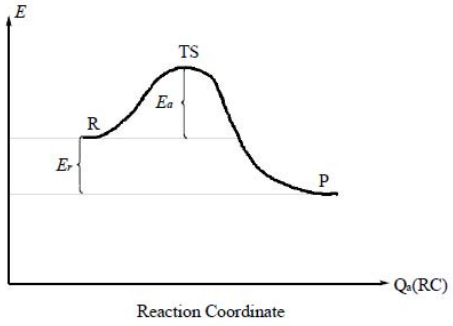
Molecule	Distortion	E_{JT}(DFT)	E_{JT}(IDP)	E_{JT}(exp)	Δ	R_{JT}	3N-6	N_{a1}
Cu_3	$D_{3h} \rightarrow C_{2v}$	**0.53** [13]	0.37	0.28-0.55 [3]	0.12	1.12	3	2
VCl_4	$T_d \rightarrow D_{2d}$	**0.04** [4, 5]	0.01	0.03-0.08 [16]	0.01	0.10	9	2
C_5H_5	$D_{5h} \rightarrow C_{2v}$	**1.25** [5]	1.24	1.24 [17]	0.00	0.17	24	9
$CoCp_2$	$D_{5h} \rightarrow C_{2v}$	**0.81** [15]	0.80	0.15-1.05 [18]	0.00	0.35	57	16
$MnCp_2$	$D_{5h} \rightarrow C_{2v}$	**0.71**[13]	0.72	~ 0.35 [18, 19]	0.00	0.77	57	16
$[Cu(en)_3]^{2+}$	$D_3 \rightarrow C_2$	**2.12** [14]	2.50	2.00 ± 0.20 [20]	0.57	2.34	105	53

Figure caption

Figure 1. Analogy between the JT distortion and the chemical reaction path: Qualitative cross section through the adiabatic potential energy surface, along JT coordinate Qa(JT), (a), and reaction coordinate Qa(RC), (b)



(a) Indication of the JT parameters: the JT stabilisation energy, E_{JT}, the warping barrier, Δ, the JT radius, R_{JT}



(b) Energy Profile along the typical chemical reaction: activation energy, E_a, reaction energy, E_r